

UMO 1528
PATENT

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03.18.03

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Van De Mark et al.
Serial No. 09/532,839
Filed March 21, 2000
Confirmation No. 7157
For WATER BORNE FILM-FORMING COMPOSITIONS
Examiner Edward J. Cain

Art Unit 1714

TO THE ASSISTANT COMMISSIONER FOR PATENTS,

SIR:

DECLARATION OF PAUL D. BLOOM UNDER 37 CFR 1.132

I, Paul D. Bloom, declare and state as follows:

1. I received a B.S. degree in Chemistry from Illinois State University in Normal, Illinois in 1996, and a Ph.D. degree in Organic Chemistry from Iowa State University in Ames, Iowa in 2001. I am currently employed as a Senior Research Scientist at Archer Daniels Midland Company. My complete academic background, professional experience, publications and honors are set forth in my curriculum vitae, attached hereto as Exhibit A.

2. I have reviewed the specification of Bumanlag, U.S. Patent No. 5,753,742, entitled "High-Solids, Aqueous, Polymeric Dispersions" filed July 31, 1996 and issued May 19, 1998. This patent generally describes high-solids aqueous emulsions which are said to be useful in the preparation of sealant, caulk, adhesive and coating

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compositions. Among other things, these compositions contain an emulsifier.

Bumanlag provides a list of exemplary emulsifiers; among them are ethylene oxide condensate of linoleic acid, lauric acid, or caproic acid. See Pat. No. 5,753,742, col. 5, lines 23-24.

3. Linoleic acid possesses two unsaturated carbon-carbon bonds and has the chemical formula $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$. Neither lauric acid nor caproic acid possess an unsaturated carbon-carbon bond: lauric acid has the formula $\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$, and caproic acid has the formula $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$. Likewise, ethylene oxide condensates of caproic acid or lauric acid do not possess an unsaturated carbon-carbon bond.

4. As shown in Blackley, *Emulsion Polymerisation: Theory and Practice*, p. 314 (1975), attached hereto as Exhibit B, the HLB (hydrophilic-lipophilic balance) value of fatty-acid ester emulsifiers may be calculated by the formula

$$\text{HLB} = 20 (1 - \text{S/A})$$

wherein S is the saponification value of the ester (i.e., the number of milligrams of potassium hydroxide required to saponify one gram of the ester) and A is the acid value of the acid (i.e., the number of milligrams of potassium hydroxide required to neutralize the acid content in one gram of the fatty acid). See also Kirk-Othmer, *Encyclopedia of*

Chemical Technology, 4th ed., vol. 23., p. 507 (1997), attached hereto as Exhibit C, which correlates the functionality of an emulsifier with its HLB value.

5. According to the formula shown above in paragraph 7, the methyl ester of linoleic acid would have an HLB value of 0.95.

6. According to the formula shown above in paragraph 7, the ethylene glycol monoester of linoleic acid would have an HLB value of 2.71.

7. According to the formula shown above in paragraph 7, the propylene glycol monoester of linoleic acid would have an HLB value of 3.43.

8. According to the formula shown above in paragraph 7, the diethylene glycol monoester of linoleic acid would have an HLB value of 4.78.


9. According to the formula shown above in paragraph 7, the dipropylene glycol monoester of linoleic acid would have an HLB value of 5.86.

10. As described in Kirk-Othmer, *Encyclopedia of Chemical Technology* (Exhibit C), to stabilize an oil-in-water emulsion, an emulsifier must have an HLB value of at least 8. When Bumanlag suggests the possibility of using ethylene oxide

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condensates of linoleic acid as an emulsifier in the aqueous emulsions he describes, therefore, it necessarily follows that he is suggesting using ethylene oxide condensates of linoleic acid other than the methyl, ethylene glycol, diethylene glycol, propylene glycol and dipropylene glycol esters of linoleic acid since each of these have an HLB value less than 8.

11. I hereby declare and state that all statements made herein are to my own knowledge true; and that all statements made on information and beliefs are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements will jeopardize the validity of the above-identified application or any patent issued thereon.


Paul D. Bloom

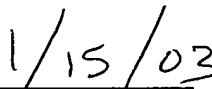

Date



EXHIBIT A

Paul D. Bloom, Ph.D.

Archer Daniels Midland Co.
James R. Randall Research Center
1001 N. Brush College Rd.
Decatur, IL 62521
bloom@admworld.com

Education

- Ph.D., Organic Chemistry, Iowa State University, Ames, IA, August 2001
- Bachelors of Science, Chemistry, Cum Laude, Illinois State University, Normal, IL, 1996

Experience

- Senior Research Scientist, Archer Daniels Midland Company, 2001-present
- Research Assistant, Iowa State University-Ames Laboratory, 1998-2001
- Ames Lab Safety Representative, 1998-2001
- Teaching Assistant, Iowa State University, Ames, IA, 1997
- Chemist I, The Valspar Corporation, Wheeling, IL, 1996-1997

Awards

- Iowa State University Research Excellence Award, Iowa State University, 2001
- Ames Laboratory Inventor Award, Ames Laboratory-USDOE, Ames, IA, 2000
- Dow Chemical Research Scholarship, Iowa State University, 2000, 1999
- Nelson Chemistry Scholarship, Iowa State University, 1997
- Robert Duty Service Award, Dept. of Chem., Illinois State University, 1996
- American Institute of Chemists Award, Illinois State University, 1996
- The Valspar Corporation Scholarship, Illinois State University, 1995
- American Chemical Society POLYED Undergraduate Research Award, 1995
- American Legion Award, 1992

Affiliations

- American Oil Chemists Society
- American Chemical Society

Selected Publications

- "Al-Cu-Fe Quasicrystal/Ultra-High Molecular Weight Polyethylene Composites as Biomaterials for Acetabular Cup Prosthetics" Anderson, B. C.; Bloom, P. D.; Baikerikar, K. G.; Sheares, V. V.; and Mallapragada, S. K. *Biomaterials*, **2002**, 23, 1761-1768.
- "Novel Poly(*p*-phenylene)s via Nucleophilic Aromatic Substitution of Poly(4'-fluoro-2,5-diphenylsulfone)" Bloom, P.D.; Sheares, V.V. *Macromolecules*, **2001**, 34(6), 1627-1633.
- "Synthesis of poly(*p*-phenylene) Macromonomers and Multiblock Copolymers" Bloom, P.D.; Sheares, V.V. *J. Polym. Sci. Part A: Polym. Chem.*, **2001**, 39(20), 3505-3512.
- "Development of Al-Cu-Fe Quasicrystal-Poly(*p*-phenylene sulfide) Composites" Bloom, P.D.; Baikerikar, K.G.; Anderegg, J.W.; Sheares, V.V. *Mat. Res. Soc. Symp. Proc.* **2001**, 643, K.16.3.1



EXHIBIT B

EMULSION POLYMERISATION

Theory and Practice

D. C. BLACKLEY

Ph.D., B.Sc., F.I.R.I.

*Reader in Polymer Science and Technology,
National College of Rubber Technology,
The Polytechnic of North London, London, England*

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NEW YORK—TORONTO

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PUBLISHED IN THE U.S.A. AND CANADA BY
HALSTED PRESS
A DIVISION OF JOHN WILEY & SONS, INC., NEW YORK

Library of Congress Cataloging in Publication Data

Blackley, D. C.

Emulsion polymerization.

"A Halsted Press book."

Includes index.

1. Polymers and polymerization. 2. Emulsions.

I. Title.

QD281.P6B447 1975 547.84 75-16336

ISBN 0-470-07740-9

WITH 134 ILLUSTRATIONS AND 88 TABLES

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Printed in Great Britain by Galliard (Printers) Ltd Great Yarmouth

PREFACE

The principal literature of emulsion polymerization is made to of writing, subject which of emulsion subject is very provide a recently published

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polymerised at 70°C using unactivated persulphate. The results were interpreted in terms of the so-called 'HLB value' of the micelle generator. The HLB value is a number which is said to quantify the 'hydrophilic-lipophilic balance' of a surface-active substance. It was first introduced by Griffin^{49,50} as a basis for predicting the behaviour of surface-active substances, and so assisting with the rational selection of appropriate types for various applications. The scale runs from 1 (indicating perfect lipophilic character) to 20 (indicating perfect hydrophilic character). Griffin⁵⁰ stresses that HLB value is not a direct measure of solubility, although there is an overall correlation in the sense that substances having low HLB values tend to be oil-soluble, whilst those having high values tend to be water-soluble. However, two substances can have the same HLB value but exhibit different solubility characteristics. Elsewhere, Griffin⁵⁰ has given the following broad correlation between HLB value and behaviour upon addition to water:

HLB range	Behaviour when added to water
1-4	No dispersibility in water
3-6	Poor dispersion
6-8	Milky dispersion after vigorous agitation
8-10	Stable milky dispersion
10-13	From translucent to clear dispersion
13+	Clear solution

The determination of HLB value is essentially empirical. It is accomplished, for example, by observing emulsifying behaviour under standardised conditions,⁴⁹ from cloud-point measurements,⁵⁰ or by calculation from chemical constitution.⁴⁹ The latter procedure is especially appropriate for non-ionogenic substances. Thus for most esters of fatty acids and polyhydric alcohols the suggested formula is

$$HLB = 20(1 - S/A)$$

where S is the saponification number of the ester and A is the acid number of the acid. For simple ethylene oxide addition products in which no polyhydric alcohol, other than the polyoxyethylene chain, is present, the suggested formula is

$$HLB = E/5$$

where E is the weight percent of ethylene oxide in the adduct. For blends of two or more surface-active substances, the HLB value of the blend is assumed⁴⁹ to be the sum of the individual values weighted according to the weight fraction of each in the blend. Thus, when Greth and Wilson present results for various properties as functions of the average HLB value of a

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EXHIBIT C

KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

FOURTH EDITION

VOLUME 23

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TO
THIN FILMS



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JOHN WILEY & SONS

New York • Chichester • Weinheim • Brisbane • Singapore • Toronto

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Library of Congress Cataloging-in-Publication Data

Encyclopedia of chemical technology/executive editor, Jacqueline

I. Kroschwitz; editor, Mary Howe-Grant. — 4th ed.

p. cm.

At head of title: Kirk-Othmer.

"A Wiley-Interscience publication."

Contents: v. 23, Sugar to thin films

ISBN 0471-52692-4 (v. 23)

I. Chemistry, Technical—Encyclopedias. I. Kirk, Raymond E.

(Raymond Eder), 1890–1937. II. Othmer, Donald F. (Donald

Frederick), 1904–1995. III. Kroschwitz, Jacqueline I., 1942–

IV. Howe-Grant, Mary, 1943– V. Title: Kirk-Othmer encyclopedia

of chemical technology.

TP9.E685:1992

91-18789

660.03—dc20

Printed in the United States of America

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Sugar
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Sulfurchlorinat
Sulfur Removal
Supercritical Flu
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Sutures
Sweeteners
Syrops

carry no discrete ionic surfactants

Oxygen atoms are ester and bonding provides a wide environment. Each oxygen atom is a single oxygen water. Nonionic surfactants. Because of ethylene oxide, a wide variety

Nonionics (ethoxylates) are formed by ether linkages in the molecule. A single ethylene oxide unit is more hydrophilic than a complete miscible mixture of water and alcohol. Ethoxylates are formed by increasing the number of ethylene oxide units in a second phase. The activity and properties of nonionics are just being affected by the presence of other surfactants. Hydrophilic-lipophilic balance (HLB) is a measure of the relative amounts of hydrophilic and lipophilic groups in a molecule. Ethoxylates are used in a wide variety of applications, including detergents, emulsifiers, and solubilizers. They are also used in the formulation of personal care products, such as shampoos and soaps. Ethoxylates are generally considered to be safe and effective for use in consumer products.

of their hydrophilic balance.

ethoxylates, the HLB number may be calculated from the following:

$$HLB = E/5$$

where E is the weight percentage of ethylene oxide in the molecule. The functionality of nonionic surfactants depends on HLB as follows:

HLB range	Application
3-6	water-in-oil (w/o) emulsifier
7-9	wetting agent
8-15	oil-in-water (o/w) emulsifier
13-15	detergent
15-18	solubilizer

Ethoxylation. Base-catalyzed ethoxylation of aliphatic alcohols, alkylphenols, and fatty acids can be broken down into two stages: formation of a monoethoxy adduct and addition of ethylene oxide to the monoadduct to form the polyoxyethylene chain. The sequence of reactions is shown in equations 20-22:



Equation 20 is the rate-controlling step. The reaction rate of the hydrophobes decreases in the order primary alcohols > phenols > carboxylic acids (84). With alkylphenols and carboxylates, buildup of polyadducts begins after the starting material has been completely converted to the monoadduct, reflecting the increased acid strengths of these hydrophobes over the alcohols. Polymerization continues until all ethylene oxide has reacted. Beyond formation of the monoadduct, reactivity is essentially independent of chain length. The effectiveness of ethoxylation catalysts increases with base strength. In practice, ratios of 0.005-0.05:1 mol of NaOH, KOH, or NaOCH₃ to alcohol are frequently used.

Alcohol Ethoxylates. These products have emerged as the principal nonionic surfactants in consumer detergent products (Table 14). Consistent quality, expanding production capacity of relatively inexpensive detergent range straight-chain, highly biodegradable alcohols, and increasing usage in laundry products, particularly heavy-duty liquids, are the principal factors underlying this growth.

Alcohol ethoxylates vary in physical form from liquids to waxes. With increasing ethylene oxide content, viscosity increases; a slight hydrophobe odor, present in the lower members of the series, decreases; specific gravity increases